A Combined Equation of State of HFC 134a

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Abstract

An equation of state (EOS) is developed in the form of the Helmholtz free energy $F(\rho,T)$ in the work to represent experimental thermodynamic data of HFC 134a in wide intervals of (ρ,T) parameters including the critical region. Known EOS' [1,2 a. o.] of HFC 134a have used analytical forms (they do not include such parameters as scaling variables and functions, critical exponents (α, β, (Δ_i) a. o.) proposed by the scaling theory (ST)), that is why they have a low accuracy in the vicinity of the critical point. $F(\rho,T)$ elaborated combines regular and non regular parts. The last one has been structured according to ST. Some criterions are involved to adobe $F(\rho,T)$ to conditions those are typical for the critical region. The adjustable coefficients of EOS have been established by a routine that let us to fit $F(\rho,T)$ to new experimental data (Blanke et al [3,4], Magee et al [5,6], Yata [7], Padua et al [8]) and known reliable results. The input data set includes thermal properties together with C_v,ρ,T – data [9].

A software program was produced for the determination of thermodynamic properties. The calculated data got with EOS are compared with experimental points and known tabulated properties. A satisfied agreement of the calculated results with literature data demonstrates that EOS recommended can successfully approximate points both in regular and singular areas. EOS can be used in intervals of parameters of state from the triple point temperature T_{tr}=169.85 K to 450 K and from the triple point pressure to 100 MPa.

Keywords: equation of state, vapour-liquid equilibrium, volume, density, vapour pressure, thermodynamic properties

1.   Introduction

Some number of investigations including [3-8] dedicates to experimental researches of thermodynamic properties of HFC 134a in regular and non regular regions of $P(\rho,T)$–surface has appeared and not been examined in the works (Tillner-Roth, Baehr [1], Dobrokhotov, Ustjuzhanin, Reutov [2]) where the international and Russian reference data are published. The information, P,ρ,T – data, P_s,T – data, ρ_l,ρ_g,T–data, C_v,ρ,T – data, is included into the input data set. An analysis of scaling conditions let us formulate some criterions and a task on a creation of EOS that is valid both in regular and critical regions of $F(\rho,T)$ surface.

2.   Criterions and EOS forms

EOS is elaborated as the Helmholtz free energy

$$F(\rho,T) = F_r(\rho,T) + F_n(\rho,T) \cdot \tag{2.1}$$

Some conditions are formulated for the scaling kernel, $F_n(\rho,T)$, according to thermodynamic equalities and ST (degree laws for derivatives of $F(\rho,T)$, a form of components $F(\rho,T)$ a. o.). $F_n(\rho,T)$ consists of three addends

$$F_n(\rho,T) = F_{na}(\rho,T) + F_{nn}(\rho,T) + F_{nas}(\rho,T). \tag{2.2}$$

It is accepted that derivatives of $F_{na}(\rho,T)$ and $F_{nn}(\rho,T)$ are to follow to degree lows in asymptotic and non asymptotic neighborhoods of the critical point, among them

$$(\partial F_{na}/\partial\rho)_T\big|_{T=T_c} \sim \Delta\rho|\Delta\rho|^{\delta-1}, \quad (\partial^2 F_{na}/\partial T^2)_\rho\big|_{T=T_c} \sim |\Delta\rho|^{-\alpha/\beta},$$

$$(\partial F_{nn}/\partial\rho)_T\big|_{T=T_c} \sim \Delta\rho|\Delta\rho|^{\delta-1+\Delta/\beta}, \quad (\partial^2 F_{nn}/\partial T^2)_\rho\big|_{T=T_c} \sim |\Delta\rho|^{(-\alpha+\Delta)/\beta}. \tag{2.3}$$

An analysis of different forms of $F(\rho,T)$ let us get an expression that obeys (2.3)

$$F(\rho,T)=F_0(T)+RT\ln\rho+RT\omega\sum_{i=1}^{n_3}\sum_{j=0}^{j_3(i)}C_{ij}\tau_1^j(\Delta\rho)^i+RT_cf(\omega)\sum_{i=0}^{n_1}\sum_{j=1}^{n_2}u_{ij}f_{ij}(t)|\Delta\rho|^{\delta+1+\Delta_i/\beta}a_i(x),\quad(2.4)$$

where $f(\omega)$ and $f_{ij}(t)$ – flattening functions, $\{a_i(x)\}$ – scale functions for the free

energy, (C_{ij}), (u_{ij}) – adjustable coefficients, R – universal gas constant.

With the use of the equality $P=\rho^2(\partial F/\partial\rho)_T$, EOS (2.4) is converted into the form of the

compressibility coefficient, $Z=P/(R\rho T)$, and expressed as

$$Z(\rho,T)=Z_r(\rho,T)+Z_n(\rho,T),\quad(2.5)$$

where $Z_r(\rho,T),Z_n(\rho,T)$ - regular and non regular parts of the second form of EOS.

The first addend in (2.5) looks like

$$Z_r(\rho,T)=1+\omega^2y_1+\omega y_2+\omega(y_3+\omega y_4)C_{10}+$$

$$+\omega(y_5+\omega y_6)C_{20}+\sum_{i=6}^{n_3}C_{i0}(\Delta\rho)^{i-1}(i\omega+\Delta\rho)+\omega\tau_1(2\omega-3)C_{11}+$$

$$+\omega^2\tau_1(3\omega-4)C_{21}+\omega\tau_1\sum_{i=3}^{n_3}C_{i1}(\Delta\rho)^{i-1}\times(i\omega+\Delta\rho)+\omega\sum_{i=0}^{n_3}\sum_{j=2}^{j_3(i)}C_{ij}\tau_1^j(\Delta\rho)^{i-1}(i\omega+\Delta\rho),\quad(2.6)$$

where (y_i)–structure functions.

(y_i) depend on $\Delta\rho$ and are determined using the conditions in the critical point

$$\left(\frac{\partial^m p}{\partial\rho^m}\right)_{v=v_c,T=Tc}=0,\quad(m=1\div4).$$

The forms of (y_i) are got as

$$y_2=-15.4/12+5.8/12(\Delta\rho)-1.1/6(\Delta\rho)^2+0.05(\Delta\rho)^3,\quad y_4=5-4\Delta\rho+3(\Delta\rho)^2-2(\Delta\rho)^3+(\Delta\rho)^4,$$

$$y_6=4-3\Delta\rho+2(\Delta\rho)^2-(\Delta\rho)^3+(\Delta\rho)^5,\quad y_1=dy_2/d\omega,\quad y_3=dy_4/d\omega,\quad y_5=dy_6/d\omega.$$

The second addend in (2.5) is obtained in the form

$$Z_n(\rho,T)=(\omega/t)\sum_{i=0}^{4}\sum_{j=1}^{n_2}u_{ij}f_{ij}(t)|\Delta\rho|^{(1-\alpha+\Delta)/\beta}g_i^*(\omega),\quad(2.7)$$

where $g_i^*(\omega) = f(\omega)sign(\Delta\rho)h_i(x) + f'(\omega)a_i(x)|\Delta\rho|^{1/\beta}$, $\{h_i(x)\}$ – scale functions for the chemical potential; $\Delta_0 = 0$, $\Delta_1 = \Delta$, $\Delta_2 = \gamma - \alpha$, $\Delta_3 = \Delta_4 = \gamma + \beta - 1$.

Scale functions $\{h_i(x)\}$ and $\{a_i(x)\}$ are connected by relations

$$h_i(x) = (\delta + 1 + \Delta_i/\beta)a_i(x) - (x/\beta)a_i'(x), \qquad i = 0...4.$$

The scale functions $\{a_i(x)\}$ have to satisfy degree lows including (2.3) and are found as

$$a_0(x) = A_1\left[\ (x + x_1)^{2-\alpha} - \frac{x_1}{x_2}(x + x_2)^{2-\alpha}\ \right] + B_1(x + x_3)^{\gamma} + C_1\ ,$$

$$a_1(x) = A_2\left[\ (x + x_4)^{2-\alpha + \Delta/\beta} - \frac{x_4}{x_5}(x + x_5)^{2-\alpha + \Delta/\beta}\ \right] + B_2(x + x_6)^{\gamma + \Delta} + C_2\ ,$$

$$a_2(x) = (x + x_7)^{2-\alpha + \Delta_2} - \frac{x_7}{x_8}(x + x_8)^{2-\alpha + \Delta_2} + C_3\ ,$$

$$a_3(x) = (x + x_9)^{\gamma + \Delta_3} + C_4,$$

$$a_4(x) = (x + x_{10})^{\gamma + \Delta_4} - (x + x_{11})^{\gamma + \Delta_4} + C_5. \qquad (2.8)$$

The coefficients, A_1, A_2, B_1, B_2, in (2.8) are expressed as equalities

$$A_1 = -\frac{k\gamma(\gamma - 1)}{2\alpha b^2(2 - \alpha)(1 - \alpha)(1 - x_1/x_2)} \ , \quad A_2 = -\frac{k(\gamma + \Delta)}{2b^2(2 - \alpha + \Delta)(1 - \alpha + \Delta)(1 - x_4/x_5)}\ ,$$

$$B_1 = B_2 = 1/(2k).$$

Characteristics k and b have the form

$$k = \left[(b^2 - 1)/x_o\right]^{\beta}, \qquad b^2 = (\gamma - 2\beta)/[\gamma(1 - 2\beta)].$$

The values (C_i) included in (2.8) are determined from equalities

$$(2 - \alpha + \Delta_i)\, a_i(x = -x_o) + x_o a_i'(x = -x_o) = 0, \qquad i = 0...4.$$

Parameters included in $\{a_i(x)\}$ have been determined by a routine and with data on the coexistence curve (CC) separately from values of adjustable coefficients, $(C_{ij}), (u_{ij})$. The numerical values of (x_i) are given in Table 1. The exponents ($\alpha, \beta, \gamma, \delta$, among them α and β are taken as effective parameters) are linked by the equalities

$$2 - \alpha = \beta(\delta + 1), \quad \gamma = \beta(\delta - 1). \qquad (2.9)$$

The flattening functions, $f(\omega)$, $(f_{ij}(t))$, are introduced in (2.7) to support a correlation of EOS with a virial row under low densities and have the form

$$f(\omega) = \left[(1-\omega^{n_4})^{n_5} - 1\right]^{n_6}, \qquad\qquad f_{ij}(t) = 1/t^{n_{ij}}. \qquad\qquad (2.10)$$

3. EOS PARAMETERS

The critical characteristics, $\rho_c, T_c, P_c, \alpha, \beta$, of EOS are considered as effective parameters. Their numerical values are determined previously by a statistical routine (see a report of the authors in the Proceedings). The coefficients, $(C_{ij}), (u_{ij})$, are to be determined with the help of a minimization routine that works with the functional, Φ,

$$\Phi = \Phi_p + \Phi_{C_v} + \Phi_{p_s} + \Phi_B + \Phi_C + \Phi_\mu, \qquad\qquad (3.1)$$

where $\Phi_p, \Phi_{C_v}, \Phi_{p_s}, \Phi_B, \Phi_C, \Phi_\mu$ – the addends those include deviations, (ΔA_i), of properties, (A_i), from calculated values, $(A_{calc\ i})$, got with EOS.

(A_i) represent such properties as P in single-phase area, C_v, P_s, the virial coefficients, B, C, and the difference of the chemical potentials, μ_l, μ_g, on CC.

A routine is produced for Φ minimization. A special attention is paid to involve C_v, ρ, T – data into the treaty together with thermal data. The values of EOS' parameters are given in Table 1.

4. Conclusion

The input data set consists of $\approx$ 2000 points placed in P, T–region from T_{tr} to 450 K and from the triple point pressure to 100 MPa. A root-mean-square (RMS) deviation, δA, of input property, A, from A_{calc} is determined with following comparison results: $\delta \rho = 0.25$ % for the densities from the input data set in the single-phase area; $\delta \rho = 0.08$ % for the density [8] under high pressures and temperatures; $\delta \rho_g = 0.9\%$ for the vapor density and $\delta \rho_l = 0.5\%$ for the liquid density on CC; $\delta \rho_l = 0.08$ % for the density [5]; $\delta \rho_l = 0.13\%$ for the results [3,4]. There are follows deviations got in the critical region: $\delta \rho_g = 0.8\%$ and $\delta \rho_l = 0.5\%$ for the densities [7].

RMS deviations of the saturation pressure are got as: δP_s =0.14 % for the data [3,4]; δP_s = 0.11 % for the results [6].

Deviations of C_v – data [9] are placed in the limits – 2.4…+3.4 % and have δC_v = 1.9%.

Table 1. Parameters of the equation of state

R=81.48886 kJ/(kg K); T_c=374.13 K; ρ_c=509.5 kg/m^3; P_c=4.051 MPa; M= 102.032 kg/kmol
α=0.1503; β=0.353; Δ=0.5
x_o=0.1222; x_1=0.6641; x_2=1.4268; x_3=0.69733; x_4=0.6952; x_5=1.4252; x_6=0.6733; x_7=0.9
x_8=1.1; x_9=1.0; x_{10}=0.9; x_{11}=1.3; n_1=4; n_2=2; n_3=15; n_4=2; n_{k1}=1, n_{k2}=2, n_{03}=3; k=0÷4
j_3(i)= {7, 4, 4, 4, 4, 4, 3, 3, 3, 3, 3, 3, 3, 3, 3}   i=1÷15

C_{31}= -0.7930946928670535,	C_{41}= -1.749327023402666,	C_{51}= -9.085398879422089,
C_{61}= -22.07980737565623,	C_{71}= 21.55533910549752,	C_{81}= 90.72614625150084,
C_{91}= 71.93572916947427,	$C_{10,1}$= 6.350466902561076,	$C_{11,1}$= -20.52180687738139,
$C_{12,1}$= -17.02794062531438,	$C_{13,1}$= -5.866953048639720,	$C_{14,1}$= 0.1166848768887534,
C_{60}= -0.1598625302561794,	C_{70}= 0.01312312878110619,	C_{80}= 1.326164614745318,
C_{90}=1.148339049592578,	$C_{10,0}$= -2.479419891106447,	$C_{11,0}$= -5.474671238416783,
$C_{12,0}$= -4.015617685331631,	$C_{13,0}$= -1.160672686432287,	$C_{14,0}$= -0.09140680969351347,
C_{12}= -.02504064253181246,	C_{13}= 0.4561012851675335,	C_{14}= -5.013025206292306,
C_{22}= -9.172058435628534,	C_{23}= 7.429247676567531,	C_{24}= 5.087652373291538,
C_{32}= 1.14274935520580,	C_{33}= 58.96628334153593,	C_{34}= 6.046420434507287,
C_{42}= 20.41055208804714,	C_{43}= 70.06640541029444,	C_{44}= 2.053594535388476,
C_{52}= -10.03960884012272,	C_{53}= -187.7440514838249,	C_{54}= -.07458502101210911,
C_{62}= -50.21286171985940,	C_{63}= -349.8711594114169,	C_{72}= 59.37798146224740,
C_{73}= -60.14288109380196,	C_{82}= 279.9383446358556,	C_{83}= 224.1809176235432,
C_{92}= 270.4375911266425,	C_{93}= 169.6484467399778,	$C_{10,2}$= 46.71863692232451,
$C_{10,3}$= 34.05223773787692,	$C_{11,2}$= -33.59242351870875,	$C_{11,3}$= -6.014450782867097,
$C_{12,2}$= -15.18555563746046,	$C_{12,3}$= -8.75657236541970,	$C_{13,2}$= -10.51667760549919,
$C_{13,3}$= -4.179165788303186,	$C_{14,2}$= 0.7623111113564205,	$C_{14,3}$= 0.3867081054609862,
C_{02}= 0.03852225917406445,	C_{03}= -4.658173168339550,	C_{04}= -3.964513646445735,
C_{05}= -14.86474810063419,	C_{06}= 3.286169428013379,	C_{07}= -.3322034540662351,
u_{01}= 0.1441935077163219,	u_{02}= 3.565866550965655,	u_{03}= 0.01598590786924933,
u_{11}= 18.87294769997517,	u_{12}= -15.37933610042395,	u_{21}= -0.8072427188327185,
u_{22}= 0.7893832845468796,	u_{31}= -21.39650517253828,	u_{32}=20.50336164122209,
u_{41}= -37.09112437100369,	u_{42}= 29.70477363358514,	C_{11}= 0.9676376578614376,
C_{21}= 0.8202885149848780,	C_{10}=0.006641891403824560	

Deviations of the virial coefficients, B,C, calculated with the help of EOS (2.5) and data [10] do not exceed the limits of ±4 % and ±2 % in a wide entire temperature range.

Calculated properties got with EOS (2.5) are compared with the reference data [1,2]. There is a satisfy agreement found between the sources in a wide regular P,T – area. Some systematic discrepancies are realized around the critical point. The difference of densities on CC [1] is

increasing up to 2% if T moves to T_c in the interval from 370 K to T_c. C_v –data calculated with

(2.5) have maximums sharply expressed on near-critical isotherms. For example present C_v

values is higher on 6 % than points (Tillner - Roth and Baehr 1994) on the isotherm T=385 K

near the maximum area. The analysis has permitted to conclude that the structure of EOS (2.5)

can be useful to approximate experimental data in a wide P,T area including thermal properties

together with C_v,ρ,T – data. Due to its form and effective scaling parameters, α,β, EOS (2.5)

has successfully approximated experimental data in the critical region. The EOS can be used to

add and correct the known data in the critical region.

List of symbols

T = temperature

P = pressure

ρ = density

P_s = saturated pressure

g,l,c = indexes to mark the vapor (liquid) phases on CC and a critical value

$F_r(\rho,T), F_n(\rho,T)$ = regular and non regular parts of EOS

$F_{na}(\rho,T), F_{nn}(\rho,T), F_{nas}(\rho,T)$ = asymptotic, non asymptotic and asymmetric components of

$F_n(\rho,T)$

$\Delta\rho = 1 - \rho_c/\rho$, $\tau = 1 - T/T_c$ = distances from the critical point

$\omega = \rho/\rho_c$ = relative density

$x = \tau/|\Delta\rho|^{1/\beta}$ = scaling variable, $x = -x_o$ = the variable, x, on CC

$\alpha,\beta,\Delta,\delta,\gamma$ = critical exponents

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